Supplementary Information:
Molecular Motion of Tethered Molecules in Bulk and Surface-Functionalized Materials: A Comparative Study of Confinement

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General. Solution-state ^{1}H and ^{13}C NMR spectroscopy were performed on Bruker 400 MHz instruments at the University of California, Berkeley (UCB). Solid-state NMR spectra were recorded at the California Institute of Technology Solid State NMR Facility. Deuterium magic angle spinning (^{2}H MAS) NMR spectra were collected on a Bruker DSX-500, with an operating frequency of 76.8 MHz, using a 4 mm Bruker double resonance probe. A 2 μs-$\pi/2$ pulse and high power ^{1}H decoupling were employed for all of the single-pulse MAS experiments. The recycle delay was 1 sec and 500 kHz of spectral sweep was used. The sample spinning rate was typically 6 kHz (± 3 Hz). About 30 min was used to reach thermal equilibrium before data acquisition for variable temperature experiments. The

changes in ^{2}H MAS NMR line shapes were analyzed using a two-site hopping motional model of the C-D bond with respect to the C-O bond axis. The simulations of NMR powder pattern under MAS were performed either by using a customized software written by Hologne and Hirshinger[53] or by calculating the time evolution of quadrupole Hamiltonian in the presence of two site exchange using MATLAB®. FAB+ mass spectra were collected at the UCB Mass Spectrometry Facility. Gas chromatography (GC) was performed on an Agilent model 6890 gas chromatograph equipped with a 30 m HP-1 column and a FID detector. Potentiometric titrations were performed using a Brinkmann/Metrohm 765 Dosimat system equipped with an Accumet AR15 pH meter and a Corning High Performance glass combination electrode with a Silver Scavenger reference. Perchloric acid in glacial acetic acid was used as the titrant. Materials were ground on a Fritsch Pulverisette 7 planetary mill. Porosimetry was performed using nitrogen physisorption at 77 K on a Quantachrome Autosorb-1 using samples that had been degassed for at least 20 hours at room temperature. All chemicals were obtained from Aldrich and used as received, unless otherwise indicated. The commercially-available monolayer of aminopropyl groups on silica was obtained from Aldrich and contained a surface coverage of 1.3 mmol/g. The Selecto 60 silica possessed a surface area of approximately 500 m^2/g, with an average pore diameter of 60 Å. The Aeroperl 300 support possessed a surface area of approximately 300 m^2/g and contained macropores with an average diameter of 400 Å.

Site Isolation. The base-catalyzed Knoevenagel condensation of isophthalaldehyde and malononitrile (Figure S1) is utilized as a probe reaction to verify site isolation in the materials of this study. The selectivity for the single-addition product over the double-addition product has been shown to be controlled by the local degree of site isolation of the catalytic active sites.[1] Nonisolated amines such as a commercially available monolayer of while isolated amines tend to stop the reaction at the single-addition product, B. As the degree of site isolation increases, so does the initial value in a plot of [C]/[B] versus conversion of A (Figure S1). The materials used in this study showed [C]/[B] ratio at or

aminopropyl groups on silica (●) promote the formation of the double-addition product, C, lower than that for the bulk imprinted material in Figure S1, which was previously shown to possess local site isolation via pyrene fluorescence experiments.[2]

Knoevenagel Condensation Catalysis. In a typical procedure for the site isolation experiments, to 19.80 g of the surface-grafted silica was added 9 mL of anhydrous benzene solution containing 0.022 M isophthalaldehyde, 0.022 M 1,3,5-trimethylbenzene internal standard, and 0.044 M malononitrile (amount of amine catalyst was fixed at 0.005 molar equivalents of amine relative to isophthalaldehyde). The reaction was performed at room temperature. In the demonstration of the mass transport characteristics of **3**, the reaction was conducted with 0.025 M isophthalaldehyde, 0.025 M 1,3,5-trimethoxybenzene internal standard, and 0.050 M malononitrile in anhydrous benzene, with 0.002 molar equivalents of amine catalyst at 40 °C. In both cases, reaction aliquots were taken by syringe and analyzed by gas chromatography.

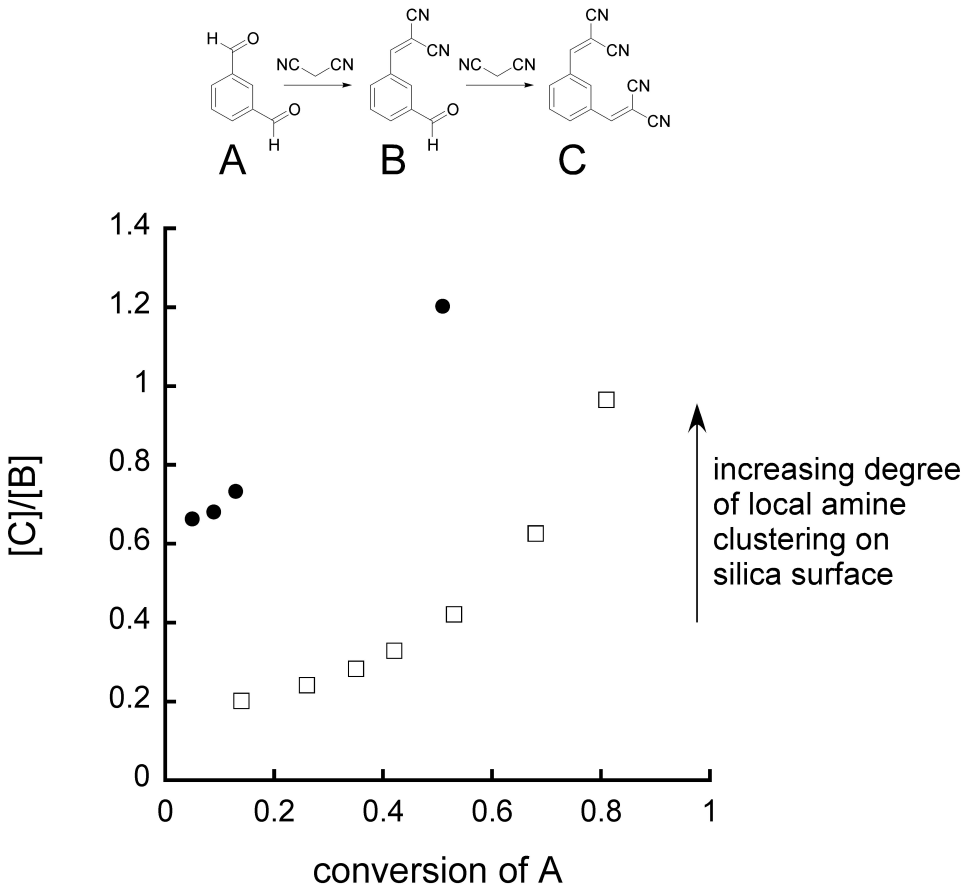

Figure S1. An example of demonstrating site isolation via the Knoevenagel condensation reaction by examining the [C]/[B] ratio. A commercially-available nonisolated monolayer of aminopropyl groups with a coverage of 1.3 mmol/g on silica (●) is compared a mesoporous bulk imprinted material (□) (similar to deprotected **3**) with a site count of 0.18 mmol/g.

Determination of hopping rate (τ_c) and quadrupole parameters. ^{2}H MAS sideband patterns were simulated with home-written software considering the two sites-hopping model as depicted below, and the resulting correlation times are given in Table 1.

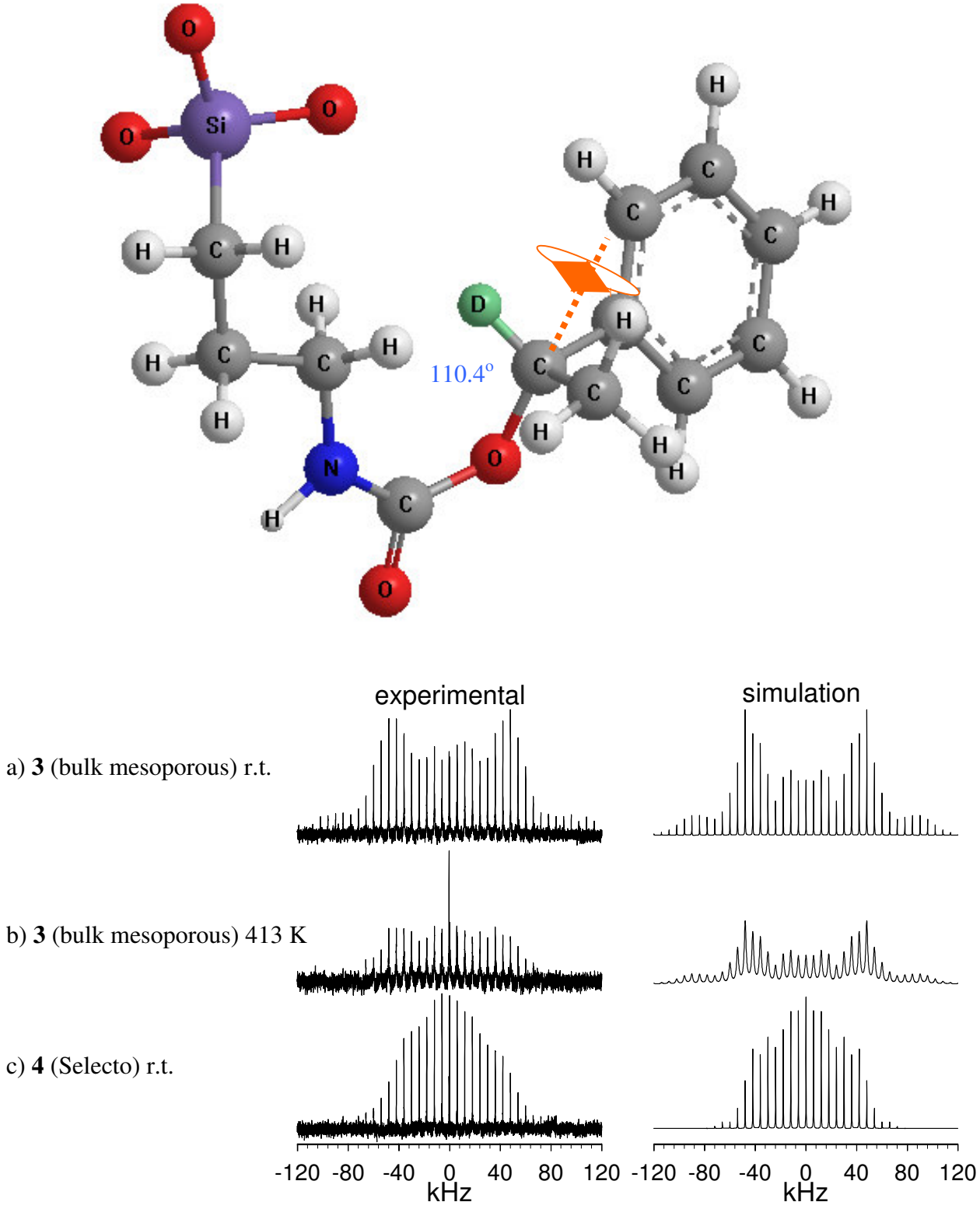

Figure S2. Experimental versus simulated spectra for the materials in the study. The jumping angle of 110-120 degrees simulates the powder patterns most reasonably. The correlation times in the spectra above are: a) $\tau_c = 10^{-2}$ s; b) $\tau_c = 10^{-3}$ s; c) $\tau_c = 10^{-9}$ s.

(1) Ini, S.; Defreese, J. L.; Parra-Vasquez, N.; Katz, A. *Mat. Res. Soc. Symp. Proc.* **2002**, *723*, 2.3.1-2.3.7.
(2) Bass, J. D.; Katz, A. *Chem. Mater.* **2003**, *15*, 2757-2763.
(3) Laupretre, F.; Monnerie, L.; Virlet, J. *Macromolecules* **1984**, *17*, 1397-1405.
(4) Pivcova, H.; Saudek, V.; Schmidt, P.; Hlavata, D.; Plestil, J.; Laupretre, F. *Polymer* **1987**, *28*, 991-997.
(5) Smith, J. M.; Dybowski, C.; Bai, S. *Solid State Nucl. Mag.* **2005**, *27*, 149-154.